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Adsorption and desorption characteristics of diphenylarsenicals in two contrasting soils

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Abstract

Diphenylarsinic acid (DPAA) is formed during the leakage of aromatic arsenic chemical weapons in soils, is persistent in nature, and results in arsenic contamination in the field. The adsorption and desorption characteristics of DPAA were investigated in two typical Chinese soils, an Acrisol (a variable-charge soil) and a Phaeozem (a constant-charge soil). Their thermodynamics and some of the factors influencing them (i.e., initial pH value, ionic strength and phosphate) were also evaluated using the batch method in order to understand the environmental fate of DPAA in soils. The results indicate that Acrisol had a stronger adsorption capacity for DPAA than Phaeozem. Soil DPAA adsorption was a spontaneous and endothermic process and the amount of DPAA adsorbed was affected significantly by variation in soil pH and phosphate. In contrast, soil organic matter and ionic strength had no significant effect on adsorption. This suggests that DPAA adsorption may be due to specific adsorption on soil mineral surfaces. Therefore, monitoring the fate of DPAA in soils is recommended in areas contaminated by leakage from chemical weapons.

Key words: diphenylarsinic acid; adsorption and desorption; chemical weapons; residual soil contamination

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Introduction

Aromatic arsenicals (AAs) were once used for the manufacture of chemical weapons such as Clark I (diphenylchloroarsine) and Clark II (diphenylcyanoarsine), which were employed as vomiting and sneezing agents during both World Wars (Arao et al., 2009). After the Second World War, chemical weapons were buried and dumped in several parts of China (Wada et al., 2006), Japan (Hanaoka et al., 2005; Ishizaki et al., 2005), Germany (Hempel et al., 2009), and Belgium (Bausinger and Preuss, 2005). The AAs can be modified by hydrolysis and oxidation, leading to the formation of diphenylarsinic acid (DPAA), which is persistent and results in arsenic contamination of soils (Nakamiya et al., 2007; Harada et al., 2010). In 2002 there was an arsenic poisoning incident in Kamisu, Japan when local people drank DPAA-contaminated well water (Ishizaki et al., 2005). Several inhabitants exhibited unusual clinical symptoms of the

central nervous system (Ishii et al., 2004). DPAA was then detected as the predominant species of arsenic in the groundwater, in which the maximum concentration was found to be 15 mg/L (Arao et al., 2009). The DPAA may have originated from illegal dumping of DPAA itself (Kinoshita et al., 2008).

Studies on the behavior of DPAA in soils are urgently required in order to fully understand its potential to exert adverse environmental effects. Arao et al. (2009) showed that DPAA can be taken up by rice and was readily transferred from the straw to the grains in a pot experiment in which rice was grown in soil amended with different forms of aromatic arsenicals. These results indicate that DPAA has some ability to transfer in the soil and can be readily absorbed by crops. Maejima et al. (2011) investigated the mobility of DPAA and its derivatives in two typical Japanese soils (a Fluvisol and an Andosol) and found that the mechanism of adsorption of DPAA was mainly due to ligand exchange reactions between variable-charge minerals and the arsenate group. AAs also appeared

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to have the potential to contaminate the groundwater by leaching.

Soils are complex systems and the fate of pollutants can exhibit different behaviors in different typical soils. There were numerous battlefields in China during the Second World War and chemical weapons were used extensively. Many locations such as the Haerbaling area in Dunhua City and Huang Huzi Mountain in Nanjing City have become contaminated through the leakage of buried chemical weapons, most of which contain large amounts of arsenicals (Tu, 2011). However, little is known about the environmental fate of DPAA in Chinese soils (Deng and Evans, 1997). Therefore, in the present study two typical Chinese soils, a Phaeozem and an Acrisol, were selected because they are widely subject to AAs leakage and they have contrasting physicochemical properties. Phaeozems are high in organic matter and are considered to be constant-charge soils. Acrisols, in contrast, contain little organic matter but have large amounts of minerals containing iron and aluminum oxides and are often referred to as variable-charge soils (Yu, 1997). Thus, our main objective was to investigate the adsorption and desorption characteristics onto these two typical Chinese soil types which often occur in areas contaminated with AAs. The effect of the soil components, initial soil pH, ionic strength and phosphate concentration on the adsorption of DPAA onto the soils were investigated to better understand the sorption mechanism and the pathways of AA movement in soils. It was hoped that the results would help to assess the potential fate of DPAA in contaminated soils.

1 Materials and methods

1.1 Chemicals

The diphenylarsenical DPAA ($C_{12}H_{11}AsO_2$, 262.14) of standard (purity 97%) was purchased from Wako Company, Osaka, Japan. The logarithm n -octanol/water partition coefficient ($\log K_{ow}$) of DPAA is 2.80, and the pK_a is 5.0 (Nakamiya et al., 2007). The acetonitrile used in quantitative analysis was of high performance liquid chromatography (HPLC) grade. Other chemicals were of analytical grade and all solutions were prepared using 18.2 M Ω Milli-Q water (Millipore Corporation, Billerica, MA).

1.2 Soil samples

Two soil types, a Phaeozem and an Acrisol, were collected from the plough layer (top 15 cm) of fields in Hailun County (Heilongjiang Province) and Yujiang County (Jiangxi province), respectively. The soil samples were air-dried and passed through a 0.25 mm sieve prior to use. Selected physico-chemical properties of the two soils are presented in **Table 1**.

1.3 Adsorption/desorption experiments

The adsorption experiments were carried out according to the batch equilibrium method. A series of DPAA solutions (2, 4, 12, 16, 20 mg/L) were prepared in 0.01 mol/L $NaNO_3$ as the background solution containing 100 mg/L NaN_3 as an anti-bacterial agent. The 2.000 g of soil was placed in a glass centrifuge tube (80 mL) with a Teflon-lined screw cap, and the whole tube was weighed as M_1 . After adding 20 mL DPAA solution at different concentrations, the pH of the mixture was adjusted according to the soil sample pH using $NaHCO_3$ solution. Previous work had shown that equilibrium can be reached in 72 hr (data not shown). The tube was shaken at 200 r/min for 72 hr at $(25 \pm 1)^\circ C$ in the dark. After centrifugation at 1500 r/min for 15 min, the supernatant was filtered through a 0.22 μm membrane filter.

The desorption experiments were conducted immediately following the adsorption experiments. The whole tube was weighed as M_2 to calculate the solution remaining in the soil after adsorption, then 20 mL of 0.01 mol/L $NaNO_3$ was added as the desorption solution and the tube was shaken again at 200 r/min for 72 hr at $(25 \pm 1)^\circ C$ in the dark. At the end point the samples were collected using the same procedure described above. All experiments were conducted in triplicate.

The amount of DPAA adsorbed on the soil sample (Q_{ads} , mg/kg), was calculated from the difference between the initial DPAA concentration (C_i , mg/L) and the equilibrium concentration (C_{eq} , mg/L) in the supernatant as follows:

$$Q_{ads} = \frac{(C_i - C_{eq}) \times V}{M} \quad (1)$$

where, V is the volume (20 mL) and M (g, dry weight basis) is the mass of the soil sample.

The amount of DPAA desorbed from the soil sample (Q_{des} , mg/kg) was calculated according to Eq. (2):

$$Q_{des} = \frac{(V_d C_d - V_r C_{eq})}{M} \quad (2)$$

where, V_d is the volume (20 mL) and C_d is the equilibrium concentration of desorption in the supernatant. V_r is the volume of adsorption equilibrium solution remaining in the soil and is equal to $M_2 - M_1$.

1.4 Effect of temperature on the adsorption of DPAA in soils

A series of DPAA solutions (2, 4, 8, 12, 16, and 20 mg/L) were prepared as described above. The 2.000 g of soil was weighed in a glass centrifuge tube, 20 mL of DPAA solution of different concentrations was added, the pH was adjusted as required, and the tube was placed on a shaker in the dark at 200 r/min for 72 hr at $(25 \pm 1)^\circ C$ and $(45 \pm 1)^\circ C$, respectively. Then the supernatants were collected as described above.

1.5 Effects of initial pH, ionic strength and phosphate on adsorption of DPAA in soils

To examine the effect of the pH value. The 2.000 g of soil was weighed in a glass centrifuge tube and 20 mL of DPAA (20 mg/L) solution was added. The pH of the soil suspension was adjusted with HCl or NaOH and the pH treatments were pH 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0. Then the tube was placed in a shaker in the dark at 200 r/min for 72 hr at $(25 \pm 1)^\circ\text{C}$. To investigate the effect of ionic strength. The 20 mg/L DPAA solutions were prepared in 0.01 and 0.1 mol/L NaNO_3 as the background solution, then the adsorption tests were carried out as described above. The effect of phosphate was determined as the following: NaH_2PO_4 was added to the 20 mg/L DPAA solution to give a P concentration of 1.0 mg/L in the solution (approximating the total content of P in the two soils). A zero-P NaH_2PO_4 control was also set up. Then 2.000 g of soil was added to the solution and the adsorption test was carried out by the procedure described above.

1.6 Analytical procedure

In other studies, measurements based on GC-MS, LC-ICP-MS or LC-MC-MS have been used to determine the concentration of aromatic arsenicals (Haas and Kripendorf, 1997; Wada et al., 2006). However, a method for determining DPAA concentrations in filtered solutions has been developed using HPLC (Shimadzu, Japan). The column used was a Shimadzu VP-ODS reversed phase C18 column (150 mm \times 4.6 mm, 5 μm). The sample injection volume was 10 μL and the mobile phase was 19% acetonitrile and 81% 0.02 mol/L KH_2PO_4 solution. The flow rate was 1 mL/min and the detector wavelength was 220 nm using a SPD-m20A detector (Shimadzu, Japan).

2 Results

2.1 Adsorption isotherms of DPAA in soils

The adsorption isotherms of DPAA onto the surfaces of Acrisol and Phaeozem are shown in Fig. 1. The amount of DPAA adsorbed on both soils increased with increasing concentration of DPAA in the starting solution and the data obtained from the batch adsorption experiments were well described by both the Freundlich model and the Henry model, all the parameters of which are presented in Table 2.

The Freundlich model can be expressed as:

$$Q_{\text{ads}} = K_f C_{\text{eq}}^n \quad (3)$$

where, K_f , the adsorption coefficient, and n , the nonlinearity factor, are the constants that give estimates of the adsorption capacity and linearity, respectively. As shown in Fig. 1, more DPAA was adsorbed on Acrisol than Phaeozem. In this study the data were also regressed to the linear Henry model to estimate the soil/water distribution coefficient (K_D) and the organic carbon adsorption coefficient K_{oc} , which represent the extent of partition of organic compounds to soils. K_{oc} can be expressed as: $K_{\text{oc}} = K_D/f_{\text{oc}}$, where, f_{oc} is the soil organic carbon content. Normalization of the K_D values results in great variation in K_{oc} values among soils. The K_{oc} value in Acrisol is 6.01 L/g and 0.04 L/g in Phaeozem. Because the K_{oc} can reflect the mobility of organic chemicals in soil, it can be concluded that DPAA was less mobile in the Acrisol than in the Phaeozem.

2.2 Desorption characteristics of DPAA from soils

Figure 2 shows the relationships between the desorption and adsorption capacities of DPAA in the soils. The amount of DPAA desorbed from the soils increased with increasing amount of DPAA adsorbed, and the data were well regressed by linear regression. The slope reflects the desorption yield in soil and a higher slope value means a lower holding capacity. According to the parameters, the slope of Acrisol (0.23) is less than that of the Phaeozem (0.66), suggesting that Acrisol can hold more DPAA than Phaeozem.

2.3 Thermodynamics of DPAA in soils

The effect of temperature on the adsorption of DPAA onto the soils is shown in Fig. 3. The data obtained were also

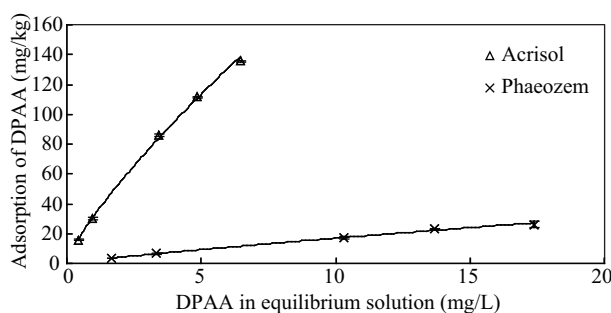


Fig. 1 Adsorption isotherms of DPAA in the two soil types. Error bars represent the standard deviation of the mean of 3 replicate samples.

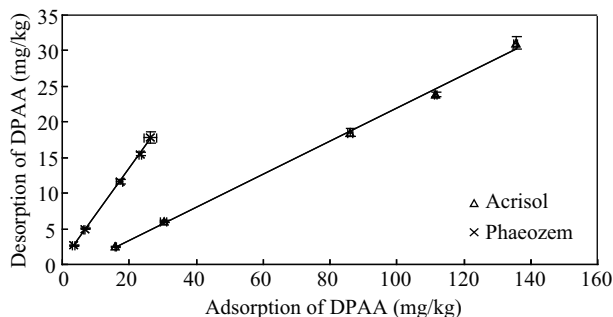
Table 1 Selected properties of the soils tested

Soil	pH ^a	OM ^b (g/kg)	CEC ^c (cmol/kg)	Free Fe ₂ O ₃ ^d (g/kg)	Total P ^e (g/kg)	Particle size distribution ^f (%)		
						Clay	Silt	Sand
Acrisol	4.6	7.5	11.8	60.9	1.19	15.5	31.5	53.6
Phaeozem	6.2	70.3	40.1	14.3	1.08	17.7	45.3	36.9

^a Ratio of soil:water was 1:10 (V/V); ^b dichromate method (Lu, 2000); ^c CEC (cation exchange capacity), ammonium acetate method (Lu, 2000); ^d DCB method (Lu, 2000); ^e aqua regia digestion; ^f the soil particle components were analyzed by Laser particle size analyzer (LS230, Beckman Coulter, USA).

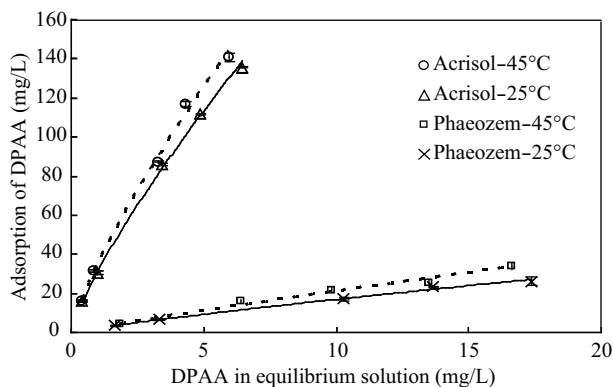
Table 2 Adsorption coefficients of DPAA in two different soils

Soil	Henry model $Q_{ads} = K_D C_{eq}$		Freundlich model $Q_{ads} = K_f C_{eq}^n$		
	K_D ((mg/kg)/(mg/L))	R^2	K_f ((mg/kg)/(mg/L) ⁿ)	n	R^2
Acrisol	20.10 (± 1.07)	0.992	31.69 (± 0.84)	0.79 (± 0.04)	0.999
Phaeozem	1.50 (± 0.08)	0.990	2.29 (± 0.38)	0.87 (± 0.06)	0.999

**Fig. 2** Relationship between the adsorption and desorption of DPAA in the two soil types. Error bars represent the standard deviation of the mean of 3 replicate samples.

fitted by the Freundlich and Henry models (**Table 3**). At low equilibrium concentration, no effect of temperature on the adsorption capacity of DPAA in the two soils was evident. The adsorption capacity was only slightly enhanced as the equilibrium concentration increased. In the Acrisol, when the temperature reached 318 K the K_f value in the Freundlich model increased from 31.69 to 35.69. The same phenomenon was also found in Phaeozem, with the K_f value increasing from 2.29 to 3.19. The insignificant temperature effect indicates that the adsorption of DPAA in soils is a spontaneous process with a low activation energy (Tiwari et al., 1999). The nonlinearity parameter n also showed no significant variations and changed only from 0.7956 to 0.7907. It may be that n , reflecting the degree of abnormality of soil particles, is independent of the temperature.

In order to fully understand the mechanism of DPAA adsorption on the soils, some thermodynamic parameters, standard Gibbs free energy ΔG^0 , enthalpy variation ΔH^0 ,

**Fig. 3** Effect of temperature on DPAA adsorption on the two soil types. Error bars represent the standard deviation of the mean of 3 replicate samples.**Table 3** Adsorption coefficients of DPAA in two different soils at 318 K

Soil	Freundlich model $Q_{ads} = K_f C_{eq}^n$		
	K_f ((mg/kg)/(mg/L) ⁿ)	n	R^2
Acrisol	35.21 (± 2.46)	0.79 (± 0.04)	0.995
Phaeozem	3.19 (± 0.76)	0.87 (± 0.09)	0.979

Table 4 Isotherm parameters and thermodynamic parameters of DPAA in different temperature

Soil	Temperature (K)	K_c	$-\Delta G^0$ (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
Acrisol	298	20.10	7.44	5.08	42
	318	22.80	8.27		
Phaeozem	298	1.50	0.99	8.84	33
	318	1.87	1.65		

entropy variation ΔS^0 , presented in **Table 4**, were calculated by the following equations (Krishna et al., 2000): $\Delta G^0 = -RT \ln K_c$ and $\Delta G^0 = \Delta H^0 - \Delta S^0 T$, where, K_c , the equilibrium constant, is equal to the K_D in the Henry model.

The negative values of ΔG^0 at all temperatures in the two soils indicate the feasibility of the process and the spontaneous nature of the DPAA adsorption onto soils. A decrease in the value of ΔG^0 with increasing temperature suggests more adsorption of DPAA at higher temperatures. However, this temperature effect was not obvious as stated above. The positive values of ΔH^0 , 5.08 kJ/mol for Acrisol and 8.84 kJ/mol for Phaeozem, imply that the adsorption of DPAA is also an endothermic process, and because of the weaker attractive forces the physisorption mechanism may play a role in this adsorption system (Tiwari et al., 1999). The positive values of ΔS^0 in the two soils reveal that the degrees of freedom increased at the solid-liquid interface during the sorption of DPAA onto the soils.

2.4 Effect of pH value on DPAA adsorption

The adsorption of DPAA in both soils decreased with increasing pH in 0.01 mol/L NaNO_3 background solution (**Fig. 4**). In Acrisol, the pH had no effect on DPAA adsorption until the pH increased from 3.0 to 6.0, then adsorption decreased markedly in high pH conditions. When the pH value was 8.0, the amount of DPAA adsorption reached 54.8 mg/L, accounting for only 40% of the normal adsorption capacity. In Phaeozem, the adsorption capacity for DPAA was also enhanced substantially in low pH conditions. When the pH was 3.0, the amount

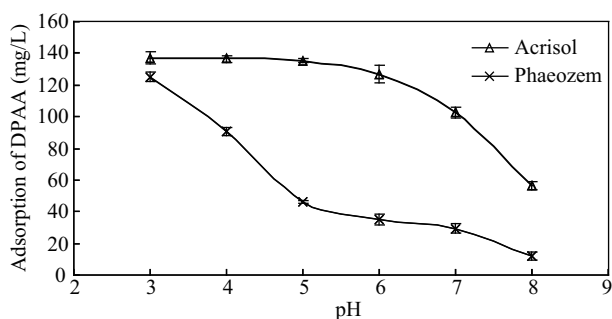


Fig. 4 Effect of pH on DPAA adsorption on the two soil types. Error bars represent the standard deviation of the mean of 3 replicate samples.

of DPAA adsorbed increased to 125.3 mg/L, which was almost as high as the adsorption capacity of DPAA in Acrisol. As the pH value increased, the adsorption capacity decreased. When the pH value changed from 5.0 to 7.0, DPAA adsorption decreased very slightly. At the end the amount adsorbed was only 12.0 mg/L.

2.5 Effect of competing ions (phosphate) and ionic strength on DPAA adsorption

It is known that phosphate adsorption on soil surfaces is similar to that of arsenate, and it is thus a strong competitor with arsenate for adsorption sites (Manning and Goldberg, 1996; Jackson and Miller, 2000; Seaman et al., 2001). The effect of phosphate was examined and is shown in **Fig. 5a**. When the phosphorus concentration in the background solution was 1 mg/L and approximately equal to the total P in the two soils (**Table 1**), DPAA adsorption in Acrisol was inhibited significantly, accounting for only 30% of the amount adsorbed on the control. However, in Phaeozem the adsorption capacity did not seem to be affected by adding phosphorus.

The effect of ionic strength on DPAA adsorption is shown in **Fig. 5b**. When the ionic strength of the solution increased to 0.1 mg/L NaNO_3 , adsorption of DPAA was unaffected in both soils.

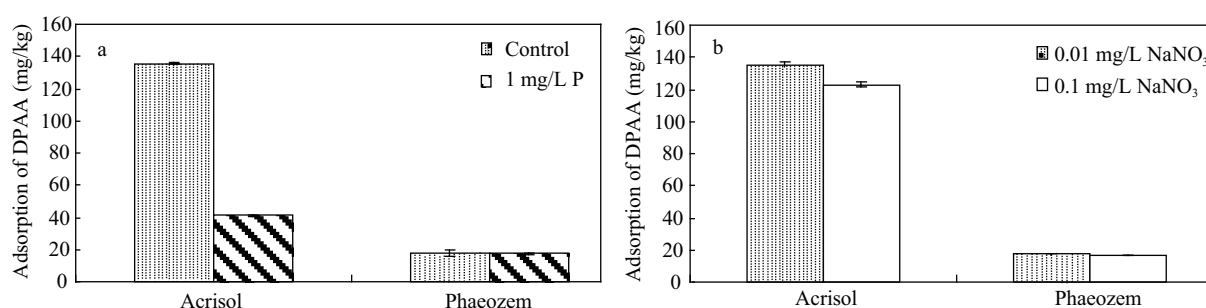


Fig. 5 Effect of phosphorus (a) and ionic strength (b) on DPAA adsorption. Error bars represent the standard deviation of the mean of 3 replicate samples.

3 Discussion

3.1 Mechanism of DPAA adsorption onto soils

The significant differences in adsorption and desorption capacity for DPAA between Acrisol and Phaeozem may be due to several factors, including the difference in soil particle size distribution, soil organic matter (OM) content, content of iron/aluminum oxides in clays, pH, and concentration of competing ions. Ljung et al. (2006) reported that the amount of As absorbed onto the soil surfaces was positively correlated with the percentage of clays. The clay distribution had no significant difference between Acrisol and Phaeozem (**Table 1**), indicating that particle size is not a major factor affecting the adsorption and desorption processes and that the functional groups may play a more important role.

In general, the adsorption mechanisms of organic compounds depend largely on their hydrophobic interactions with soil organic matter (Rutherford et al., 1992; Spark and Swift, 2002; Nguyen et al., 2005), especially in the case of non-ionic organic compounds (Chiou et al., 1984; Ying and Kookana, 2005; Xu et al., 2009). However, adsorption of ionic organic compounds is influenced to a greater extent by ligand exchange. Several lines of evidence in the present study suggest that the adsorption mechanism of DPAA onto soil was controlled by the arsenate functional group rather than phenyl (Mader et al., 1997). When the two soil types are compared, Acrisol has a higher content of free iron oxides but Phaeozem has a much higher soil organic matter content. As described above, the K_{oc} value of Acrisol was 6.01 L/g, significantly higher than that of Phaeozem at 0.04 L/g. During the desorption process, Phaeozem was unable to retain DPAA. Furthermore, higher temperatures did not lead to any significant increase in the DPAA adsorption capacity of either soil. All these results indicate that high soil OM content made little contribution to the adsorption of DPAA, and the amount of DPAA sorbed on soils appears to be correlated to the content of free iron oxides. This finding is similar to the results of Maejima et al. (2011) who reported that some AAs (including DPAA) were sorbed strongly on high variable charge soil, although the soil had a high soil OM content. When soil OM was removed, thereby exposing

the iron/aluminum oxides, the DPAA adsorption capacity was enhanced and it was concluded that the adsorption of DPAA may be due to ligand exchange.

As discussed above, arsenate forms inner-sphere complexes with Fe/Al oxides. This is a strong form of bonding and belongs to the specific adsorption category (Goldberg, 1986; Waltham and Eick, 2002; Luo et al., 2006; Catalano et al., 2007). This charge-dependent adsorption is greatly affected by changes in soil pH (Grossl et al., 1997; Xu et al., 2009). As noted above, the uptake of DPAA decreased with increasing pH for both soils. It may be proposed that at lower pH the arsenate groups on the DPAA were in both uncharged species and anionic species (according to the pK_a of DPAA), and also the soil surface released hydroxyl groups and became positively charged, which would facilitate the adsorption of DPAA onto the soil surfaces through both surface complexation and the van der Waals attraction (Lee and Tiwari, 2012; Tiwari and Lee, 2012). However, at higher pH the surface became negatively charged in addition to the DPAA being negatively charged, and they were repelled by each other, so that the sorption of DPAA was hampered. Results also show that phosphate, a known competitor with arsenate in adsorption onto soil particles (Pigna et al., 2006), showed strong inhibition of DPAA adsorption in Acrisol, suggesting that adsorption of DPAA may be a form of specific adsorption. However, phosphate had little effect on DPAA adsorption in Phaeozem. It is possible that the high soil OM content of Phaeozem inhibited the specific adsorption sites and thus adsorption was unaffected by phosphate. The effect of ionic strength in the solution on changing anion partitioning can distinguish between specific and non-specific adsorption (Hayes et al., 1988; Antelo et al., 2005; Xu et al., 2009). Specific adsorption is unaffected by changes in ionic strength, but non-specific adsorption is likely to be influenced greatly by changes in ionic strength because of the competitive adsorption with counter ions. The adsorption capacity of DPAA was not affected by increasing ionic strength in these two soils. Thus, the DPAA adsorption process was mainly governed by specific adsorption and because of the phenyl groups, the bonding characteristics of the arsenate groups with mineral clays was altered significantly, similar to the changes that have been found to occur in other organic arsenicals (Jing et al., 2005; Lafferty and Loepfert, 2005). In addition, because of the low Gibbs free energy in the adsorption process, DPAA adsorption is a physisorption process.

3.2 Mobility of DPAA in soils

Understanding the sorption behavior of DPAA on soils is important to access its mobility in soil systems and potential impacts on the environment. Roxarsone, which also contains a phenyl group and an arsenate group, was once considered to be resistant to degradation and was used in some countries as an additive in poultry feed for

prevention of coccidiosis and for growth stimulation (Anderson, 1983). However, recent studies have reported that roxarsone is a major source of total As in soils, sediments and groundwater due to its high mobility, which increases further when roxarsone is biologically transformed into inorganic arsenate or arsenite (Arai et al., 2003; Brown et al., 2005). DPAA has also been found to be degraded in soil, although the process is slow (Maejima et al., 2011). In the present study in typical Chinese soils the holding capacity of DPAA was weaker, even in Acrisol with high content of iron/aluminum oxides, than inorganic arsenic and other methyl arsenicals (Huang et al., 2011), according to the Gibbs free energy obtained (Table 4). Moreover, the soil OM content reduced the immobilizing capacity. This suggests that in northeast China, where most of the chemical weapon leakage accidents have occurred and most of the soils are of Phaeozem type, it is necessary to monitor soil, water and crop DPAA levels in areas contaminated with chemical weapons. In addition, in other areas, arable soils should also be monitored because the application of phosphate to DPAA-contaminated soils for crop production may enhance the mobility of DPAA and result in highly adverse environmental risk to the human food chain.

4 Conclusions

The adsorption and desorption characteristics of DPAA were demonstrated in two typical but contrasting Chinese soils. DPAA adsorption was found to be strongly associated with soil iron/aluminum oxide content, and could be affected by soil pH and phosphate status. The adsorption mechanism was mainly due to specific adsorption. Because of its poor adsorption capacity in soils due to soil OM and phosphate, DPAA represents a threat to the terrestrial environment, and its fate in soils contaminated by chemical weapon leakage fields requires further study and monitoring to minimize harmful effects to the environment and the human population.

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References

- Anderson C, 1983. Arsenicals as feed additives for poultry and swine. In: Arsenic-Industrial, Biomedical, Environmental Perspectives (Lederer W, Fensterheim R, eds.). Van Nostrand Reinhold Co., New York. 89–97.
- Antelo J, Avena M, Fiol S, Lopez R, Arce F, 2005. Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *Journal of Colloid*

- and *Interface Science*, 285(2): 476–486.
- Arai Y, Lanzarotti A, Sutton S, Davis J A, Sparks D L, 2003. Arsenic speciation and reactivity in poultry litter. *Environmental Science and Technology*, 37(18): 4083–4090.
- Arao T, Maejima Y, Baba K, 2009. Uptake of aromatic arsenicals from soil contaminated with diphenylarsinic acid by rice. *Environmental Science and Technology*, 43(4): 1097–1101.
- Bausinger T, Preuss J, 2005. Environmental remnants of the first World War: Soil contamination of a burning ground for arsenical ammunition. *Bulletin of Environmental Contamination and Toxicology*, 74(6): 1045–1052.
- Brown B L, Slaughter A D, Schreiber M E, 2005. Controls on roxarsone transport in agricultural watersheds. *Applied Geochemistry*, 20(1): 123–133.
- Catalano J G, Zhang Z, Park C Y, Fenter P, Bedzyk M J, 2007. Bridging arsenate surface complexes on the hematite (012) surface. *Geochimica Et Cosmochimica Acta*, 71(8): 1883–1897.
- Chiou C T, Porter P E, Shoup T D, 1984. Partition equilibria of nonionic organic-compounds between soil organic-matter and water. *Environmental Science and Technology*, 18(4): 295–297.
- Deng H M, Evans P O M, 1997. Social and environmental aspects of abandoned chemical weapons in China. *The Nonproliferation Review*, 4(3): 101–108.
- Goldberg S, 1986. Chemical modeling of arsenate adsorption on aluminum and iron-oxide minerals. *Soil Science Society of America Journal*, 50(5): 1154–1157.
- Grossl P R, Eick M, Sparks D L, Goldberg S, Ainsworth C C, 1997. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. *Environmental Science and Technology*, 31(2): 321–326.
- Haas R, Krippendorf A, 1997. Determination of chemical warfare agents in soil and material samples: Gas chromatographic analysis of phenylarsenic compounds (sternutators) (1st communication). *Environmental Science and Pollution Research International*, 4(3): 123–124.
- Hanaoka S, Nagasawa E, Nomura K, Yamazawa M, Ishizaki M, 2005. Determination of diphenylarsenic compounds related to abandoned chemical warfare agents in environmental samples. *Applied Organometallic Chemistry*, 19(2): 265–275.
- Harada N, Takagi K, Baba K, Fujii K, Iwasaki A, 2010. Biodegradation of diphenylarsinic acid to arsenic acid by novel soil bacteria isolated from contaminated soil. *Biodegradation*, 21(3): 491–499.
- Hayes K F, Papelis C, Leckie J O, 1988. Modeling ionic-strength effects on anion adsorption at hydrous oxide solution interfaces. *Journal of Colloid and Interface Science*, 125(2): 717–726.
- Hempel M, Daus B, Vogt C, Weiss H, 2009. Natural attenuation potential of phenylarsenicals in anoxic groundwaters. *Environmental Science and Technology*, 43(18): 6989–6995.
- Huang J H, Hu K N, Decker B, 2011. Organic arsenic in the soil environment: speciation, occurrence, transformation, and adsorption behavior. *Water Air and Soil Pollution*, 219(1–4): 401–415.
- Ishii K, Tamaoka A, Otsuka F, Iwasaki N, Shin K, Matsui A et al., 2004. Diphenylarsinic acid poisoning from chemical weapons in Kamisu, Japan. *Annals of Neurology*, 56(5): 741–745.
- Ishizaki M, Yanaoka T, Nakamura M, Hakuta T, Ueno S, Komura M et al., 2005. Detection of bis(diphenylarsine)oxide, diphenylarsinic acid and phenylarsonic acid, compounds probably derived from chemical warfare agents, in drinking well water. *Journal of Health Science*, 51(2): 130–137.
- Jackson B P, Miller W P, 2000. Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides. *Soil Science Society of America Journal*, 64(5): 1616–1622.
- Jing C Y, Meng X G, Liu S Q, Baidas S, Patraju R, Christodoulatos C et al., 2005. Surface complexation of organic arsenic on nanocrystalline titanium oxide. *Journal of Colloid and Interface Science*, 290(1): 14–21.
- Kinoshita K, Noguchi A, Ishii K, Tamaoka A, Ochi T, Kaise T, 2008. Urine analysis of patients exposed to phenylarsenic compounds via accidental pollution. *Journal of Chromatography B—Analytical Technologies in the Biomedical and Life Sciences*, 867(2): 179–188.
- Krishna B S, Murty D S, Jai Prakash B S, 2000. Thermodynamics of chromium(VI) anionic species sorption onto surfactant-modified montmorillonite clay. *Journal of Colloid and Interface Science*, 229(1): 230–236.
- Lafferty B J, Loeppert R H, 2005. Methyl arsenic adsorption and desorption behavior on iron oxides. *Environmental Science and Technology*, 39(7): 2120–2127.
- Lee S M, Tiwari D, 2012. Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Applied Clay Science*, 59–60: 84–102.
- Ljung K, Selinus O, Ottaabong E, Berglund M, 2006. Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry*, 21(9): 1613–1624.
- Lu R K, 2000. *Analytical Methods for Soil and Agrochemistry*. Agricultural Science and Technology Press, Beijing.
- Luo L, Zhang S Z, Shan X Q, Jiang W, Zhu Y G, Liu T et al., 2006. Arsenate sorption on two Chinese red soils evaluated with macroscopic measurements and extended X-ray absorption fine-structure spectroscopy. *Environmental Toxicology and Chemistry*, 25(12): 3118–3124.
- Mader B T, Goss K U, Eisenreich S J, 1997. Sorption of non-ionic, hydrophobic organic chemicals to mineral surfaces. *Environmental Science and Technology*, 31(4): 1079–1086.
- Maejima Y, Arao T, Baba K, 2011. Transformation of diphenylarsinic acid in agricultural soils. *Journal of Environmental Quality*, 40(1): 76–82.
- Maejima Y, Murano H, Iwafune T, Arao T, Baba K, 2011. Adsorption and mobility of aromatic arsenicals in Japanese agricultural soils. *Soil Science and Plant Nutrition*, 57(3): 429–435.
- Manning B A, Goldberg S, 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Science Society of America Journal*, 60(1): 121–131.
- Nakamiya K, Nakayama T, Ito H, Edmonds J S, Shibata Y, Morita M, 2007. Degradation of arylarsenic compounds by microorganisms. *FEMS Microbiology Letters*, 274(2): 184–188.
- Nguyen T H, Goss K U, Ball W P, 2005. Polyparameter linear

- free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. *Environmental Science and Technology*, 39(4): 913–924.
- Pigna M, Krishnamurti G S R, Violante A, 2006. Kinetics of arsenate sorption-desorption from metal oxides: Effect of residence time. *Soil Science Society of America Journal*, 70(6): 2017–2027.
- Rutherford D W, Chiou C T, Kile D E, 1992. Influence of soil organic-matter composition on the partition of organic-compounds. *Environmental Science and Technology*, 26(2): 336–340.
- Seaman J C, Arey J S, Bertsch P M, 2001. Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *Journal of Environmental Quality*, 30(2): 460–469.
- Spark K M, Swift R S, 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. *Science of the Total Environment*, 298(1-3): 147–161.
- Tiwari D, Lee S M, 2012. Novel hybrid materials in the remediation of ground waters contaminated with As(III) and As(V). *Chemical Engineering Journal*, 204-206: 23–31.
- Tiwari D, Mishra S P, Mishra M, Dubey R S, 1999. Biosorptive behaviour of Mango (*Mangifera indica*) and Neem (*Azadirachta indica*) bark for Hg^{2+} , Cr^{3+} and Cd^{2+} toxic ions from aqueous solutions: a radiotracer study. *Applied Radiation and Isotopes*, 50(4): 631–642.
- Tu A T, 2011. Chemical weapons abandoned by the Imperial Japanese Army in Japan and China at the end of World War II. *Toxin Reviews*, 30(1): 1–5.
- Wada T, Nagasawa E, Hanaoka S, 2006. Simultaneous determination of degradation products related to chemical warfare agents by high-performance liquid chromatography/mass spectrometry. *Applied Organometallic Chemistry*, 20(9): 573–579.
- Waltham C A, Eick M J, 2002. Kinetics of arsenic adsorption on goethite in the presence of sorbed silicic acid. *Soil Science Society of America Journal*, 66(3): 818–825.
- Xu J, Chen W P, Wu L S, Chang A C, 2009a. Adsorption and degradation of ketoprofen in soils. *Journal of Environmental Quality*, 38(3): 1177–1182.
- Xu R K, Wang Y, Tiwari D, Wang H Y, 2009b. Effect of ionic strength on adsorption of As(III) and As(V) on variable charge soils. *Journal of Environmental Sciences-China*, 21(7): 927–932.
- Ying G G, Kookana R S, 2005. Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. *Environmental Toxicology and Chemistry*, 24(10): 2640–2645.
- Yu T R, 1997. *Chemistry of Variable Charge Soils*. Oxford University Press, New York.

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